Secondary iron mineral identification upon Fe(II) sorption on montmorillonite

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Introduction

Smectite clay minerals are used for a range of industrial purposes including as a barrier to isolate waste from the environment. In the latter subsurface scenario it is anticipated that ferrous iron will interact with these clay barriers. A variety of secondary iron minerals have been observed to form when aqueous Fe(II) interacts with smectite clay minerals and this can impact upon the chemical reduction of waste contaminants. The aim of this study was to evaluate the effect of pH and background electrolyte anions on the nature of the major secondary iron minerals that form when Fe(II) interacts with an Australian montmorillonite clay mineral.

Experimental Methods

The montmorillonite used in this study was sourced from Miles, QLD, Australia. It was size-fractionated to <2 μm, Na^+ saturated, washed and freeze-dried. Batch experiments were performed under anoxic conditions between pH 6.5 to 8 using Cl^-, SO_4^{2-} or HCO_3^- as the major background electrolyte anion. These anions can act as the interlayer anion in green rust minerals. The degree of Fe(II) sorption and reduction potential of the samples were monitored up to 21 days. Samples were periodically taken and dried anoxically for XAS analyses. XAS data were collected on the XAS beamline at the Australian Synchrotron using a Si(311) monochromator. Linear combination fitting was used to determine the speciation of iron in the samples.

Results and Discussion

In all cases, Fe(II) sorption resulted in electron transfer to structural Fe(III) in montmorillonite. At pH values ≤ 7, ferrihydrite was the only secondary mineral observed to form. It was also the dominant mineral at pH 7.5 when SO_4^{2-} was the major background electrolyte anion. However, in the other two cases, green rust became the dominant secondary mineral at pH values ≥ 7.5 with it also forming in the sulfate system at pH 8. The formation of this mineral only occurred when Fe(II) uptake resulted in an additional 50 % increase or more in solid-phase Fe concentrations. Due to aqueous complexation by sulfate, Fe(II) uptake by montmorillonite was inhibited resulting in green rust forming at higher pH values.

Conclusions

This study demonstrates that Fe(II) sorption to montmorillonite has the potential to template for the neo-formation of green rust at pH values ≥ 7.5 in relevant anoxic continental or marine environments. This newly uncovered pathway to green rust formation offers a possible explanation as to why this mineral, a very powerful reductant, was first discovered under natural conditions in hydromorphic soils that are naturally rich in montmorillonite.